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(54) WATER-DILUTABLE TWO-COMPONENT COATING COMPOSITION, A
PROCESS FOR ITS PREPARATION, AND THE USE THEREOF(54) COMPOSITION DE REVETEMENT EN DEUX PARTS SOLUBLE DANS L'EAU,
PROCÉDE DE PRÉPARATION ET UTILISATION DE LADITE COMPOSITION[View or Download Images](#)

ABSTRACT:

Water-dilutable two-component coating composition comprising an isocyanate component having a viscosity at 23°C of from 50 to 10,000 mPa.s including one or more organic polyfunctional isocyanates, and an alkyd resin emulsion whose solid component comprises in each case proportions by mass of from 60 to 98% of an alkyd resin and from 2 to 40% of a hydroxy-functional emulsifier and which optionally comprises proportions by mass of organic solvents of up to 15%, based on the mass of the emulsion, the remainder of the emulsion being water. The coatings are useful, for example, as clearcoat, basecoat, or topcoat compositions.

CLAIMS: [Show all claims](#)

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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2175530

Abstract of the Disclosure

Water-dilutable two-component coating composition comprising an isocyanate component having a viscosity at 23°C of from 50 to 10,000 mPa·s including one or more
5 organic polyfunctional isocyanates, and an alkyd resin emulsion whose solid component comprises in each case proportions by mass of from 60 to 98% of an alkyd resin and from 2 to 40% of a hydroxy-functional emulsifier and which optionally comprises proportions by mass of organic
10 solvents of up to 15%, based on the mass of the emulsion, the remainder of the emulsion being water. The coatings are useful, for example, as clearcoat, basecoat, or topcoat compositions.

What Is Claimed Is:

1. A water-dilutable two-component coating composition comprising:

(a) an isocyanate component having a viscosity at 23°C of from 50 to 10,000 mPa·s, comprising one or more organic polyfunctional isocyanates; and

(b) an alkyd resin aqueous emulsion whose solid component comprises in each case a mass fraction of

(b1) from 60 to 98% of one or more alkyd resins and

(b2) from 2 to 40% of one or more hydroxy-functional emulsifiers,

and where component (b) further comprises

(b3) optionally, up to 15%, based on the mass of emulsion, of organic solvents, and

(b4) water.

2. A water-dilutable two-component coating composition as claimed in claim 1, wherein the isocyanate component (a) has a mean isocyanate functionality of from 2.2 to 5.

3. A water-dilutable two-component coating composition as claimed in claim 1, wherein the ratio of the number of isocyanate groups in component (a) to the number of hydroxyl groups in the alkyd resin (b1) is from 0.3:1 to 5:1.

4. A water-dilutable two-component coating composition as claimed in claim 1, wherein the isocyanate component (a) comprises one or more diisocyanate derivatives with structures selected from biuret, urethane, uretdione, and isocyanurate structures.

5. A water-dilutable two-component coating composition as claimed in claim 1, wherein the polyfunctional isocyanates contain only aliphatic structures.

6. A water-dilutable two-component coating composition as claimed in claim 1, wherein the isocyanate component (a) contains less than 0.5% of monomeric diisocyanates.

7. A water-dilutable two-component coating composition as claimed in claim 1, wherein the isocyanate component contains a mass fraction of at least 5% of a polyfunctional isocyanate which is obtained by reacting a diisocyanate with a hydrophilic component containing at least two isocyanate-reactive groups and at least one group selected from polyoxyethylene groups, polyoxypropylene groups, ionic groups, or ionogenic groups.

8. A water-dilutable two-component coating composition as claimed in claim 1, wherein the polyfunctional isocyanates comprise one or more sterically hindered diisocyanates having 4 to 25 carbon atoms.

9. A water-dilutable two-component coating composition as claimed in claim 1, wherein the mass fraction of saturated and unsaturated fatty acids in the alkyd resin component (b1) is from 10 to 80% of the mass of the alkyd resin.

10. A water-dilutable two-component coating composition as claimed in claim 1, wherein the mass fraction of saturated and unsaturated fatty acids in the alkyd resin component (b1) is from 20 to 70% of the mass of the alkyd resin.

11. A water-dilutable two-component coating composition as claimed in claim 1, wherein the mass fraction of polyoxyalkylene groups in the solid component of the alkyd resin emulsion is not more than 20%.

12. A water-dilutable two-component coating composition as claimed in claim 1, wherein the emulsifier component (b2) is a hydroxy-functional polyurethane-polyurea dispersion.

13. A water-dilutable two-component coating composition as claimed in claim 1, wherein the emulsifier component (b2) is obtained by chain extension of a polyethylene glycol-containing, isocyanate-functional prepolymer in the aqueous phase, using one or more polyamines.

14. A process for the preparation of coating composition as claimed in claim 1, which comprises in a first step transferring alkyd resin (b1) to the aqueous phase with the aid of hydroxy-functional emulsifiers (b2), and then emulsifying a polyisocyanate component (a) in this emulsion.

15. A substrate coated with an aqueous two-component coating composition as claimed in claim 1.

16. A multilayer coating, wherein at least one of the layers is formed from two-component coating composition as claimed in claim 1.

17. A single-coat finish or topcoat comprising a coating composition as claimed in claim 1.

18. A primer comprising a composition as claimed in claim 1.

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WATER-DILUTABLE TWO-COMPONENT COATING COMPOSITION
A PROCESS FOR ITS PREPARATION, AND THE USE THEREOF

Background of the Invention

Field of the Invention

5 The invention relates to an aqueous coating composition, especially a two-component aqueous coating composition, to a process for its preparation, and to its use in single-coat and multicoat systems.

Description of Detailed Art:

10 On the basis of their outstanding properties, prior art two-component polyurethane coating materials are of great importance in the coatings sector. A disadvantage, however, is that relatively large quantities of organic solvents are required for processing, which must be
15 removed by, for example, incineration. In many areas of application, especially outside industry, such incineration is impracticable, so that there is increased demand here for high-solids yet, in particular, water-dilutable coatings, in order to minimize the emission of solvent
20 and the associated environmental pollution.

 The use of water as liquid phase in two-component polyurethane coating materials having free isocyanate groups is in general not readily possible, since isocyanate groups react not only with alcoholic hydroxyl
25 groups but also with water to form N-substituted polyurea compounds, giving off carbon dioxide as they do so. Because of this, in general, the service life, pot life and quality of the coatings are reduced to levels incompatible with their practical use. Nevertheless,
30 much effort has recently been expended in attempting to overcome these disadvantages.

 For instance, DE-A 42 26 243 describes an aqueous two-component coating composition based on

polyisocyanates and on self-emulsifying, fatty acid-modified polyesters and polyurethanes. European Patent Application EP-A 0 496 205, as well describes aqueous binder combinations based on polyisocyanates and self-emulsifying polyester resins which possess urethane, carboxyl and hydroxyl groups. DE-C 31 22 030 describes coating compositions comprising polyisocyanate and water-dilutable alkyd, melamine and acrylic resins, which compositions also comprise water-miscible solvents.

Disadvantages of the above-described water-dilutable two-component binders is the low achievable solids content, the relatively low boil limit, and the short pot life.

Summary of the Invention

It was therefore an object of the present invention to provide water-dilutable two-component binders that improve on those already known.

It has surprisingly now been found that selected, externally emulsified alkyd resins, which are described in more detail below, are particularly suitable, outstanding emulsifying partners for combination with nonblocked polyisocyanate curing agents, and are distinguished by high solids contents, good pot lives, and high boil limits.

The invention therefore provides a water-dilutable two-component coating composition comprising

- (a) a polyisocyanate component having a viscosity at 23°C of from 50 to 10,000 mPa·s, including one or more organic polyfunctional isocyanates, and
- (b) an alkyd resin emulsion whose solid component comprises in each case a mass fraction of
 - (b1) from 60 to 98% of one or more alkyd resins and
 - (b2) from 2 to 40% of one or more hydroxy-functional emulsifiers, and which comprises

(b3) if desired, up to 15%, based on the mass of emulsion, of organic solvents, and also (b4) water.

5 The invention also provides a process for the preparation of coating compositions composed of an aqueous binder combination with or without auxiliaries and additives which are known from coatings technology, which comprises first transferring the alkyd resin to the aqueous phase with the aid of emulsifiers and then
10 emulsifying into the aqueous emulsion of the alkyd resin a polyisocyanate component having a viscosity at 23°C of from 50 to 10,000 mPa·s and which includes at least one organic polyisocyanate. In this process, the proportions of the two components are preferably chosen such that the
15 ratio of the number of isocyanate groups in the polyisocyanate component to the number of hydroxyl groups in the alkyd resin is from 0.3:1 to 5:1. The auxiliaries and additives used if desired are generally incorporated into the externally emulsified alkyd resin emulsion prior
20 to the addition of the polyisocyanate component.

Also, the invention additionally provides for the use of the novel binder combinations as binders, for example, for paints, coating compositions, and sealing compounds.

25 Further objects, features, and advantages of the present invention will become apparent from the detailed description of the preferred embodiments that follows.

Throughout this specification, the term "high solids content" refers to mass fractions of solids of more than 50%, preferably more than 55%, and particularly
30 preferably more than 60%. "Long pot life" means a pot life of at least 2 hours, preferably of at least 4 hours.

Detailed Description of the Preferred Embodiments

The polyisocyanate component (a) comprises any desired organic polyisocyanates having at least two
35 isocyanate groups per molecule, particularly those which are liquid at room temperature and, generally, whose isocyanate groups are in each case bonded to an aliphatic, cycloaliphatic, araliphatic, or aromatic

carbon atom. In general the polyisocyanate component (a) has a viscosity of from 50 to 10,000 mPa·s, preferably from 50 to 1000 mPa·s, at 23°C. It is particularly preferably a polyisocyanate or polyisocyanate mixture
5 containing only aliphatically and/or cycloaliphatically bonded isocyanate groups and having a (mean) NCO functionality of between 2.2 and 5.0 and a viscosity at 23°C of from 50 to 500 mPa·s.

The polyisocyanates can if required or desired be
10 used as a blend with small quantities of inert solvents, in order to reduce the viscosity to a value within the stated ranges. However, the quantity of such solvents is preferably calculated such that, in the novel coating compositions ultimately obtained, the mass of solvents is
15 not more than 20% of the mass of water, this calculation includes any solvents which may still be present in the alkyd resin emulsion. Examples of solvents suitable for addition to the polyisocyanates are aromatic or aliphatic hydrocarbons, such as, for example, "Isopar® H", ketones,
20 esters or aprotic water-miscible solvents, for example N-methylpyrrolidone.

Polyisocyanates particularly suitable as component (a) are the so-called paint polyisocyanates having aromatically or (cyclo)aliphatically bonded isocyanate
25 groups; in this context, the latter aliphatic polyisocyanates are, as already mentioned, particularly preferred. It is preferred to employ only isocyanates derived from aliphatic polyfunctional isocyanates.

Highly suitable examples are paint polyisocyanates
30 derived from hexamethylene diisocyanate, 1-isocyanato-3,3,5-trimethyl-4-isocyanatomethylcyclohexane (IPDI) and bis(isocyanatocyclohexyl)methane, especially hexamethylene diisocyanate. "Paint polyisocyanates" based on these diisocyanates are to be understood as being the
35 derivatives of these diisocyanates which are known per se, comprise biuret, urethane, uretdione and/or isocyanurate groups and, following their preparation, have been freed in a known manner, preferably by distillation, from excess initial diisocyanate down to a

residual content of less than 0.5% by mass. Particularly preferred paint polyisocyanates are those which are completely free of monomer fractions.

Preferred aliphatic polyisocyanates to be used in accordance with the invention include the hexamethylene diisocyanate-based, biuret-containing polyisocyanates which meet the above criteria, as can be obtained, for example, by the processes of U.S. Patents No. 3,124,605; No. 3,358,010; No. 3,903,126; No. 3,903,127; and No. 3,976,622 (all hereby incorporated by reference), which comprise mixtures of N,N,N-tris(6-isocyanatohexyl)-biuret with minor amounts of its higher homologs, and the cyclic hexamethylene diisocyanate trimers which meet the above criteria, as can be obtained in accordance with U.S. Patent No. 4,324,879 (hereby incorporated by reference), which essentially comprise N,N,N-tris(6-isocyanatohexyl) isocyanurate in a mixture with minor amounts of its higher homologs. Particular preference is given to mixtures which meet the criteria specified and comprise hexamethylene diisocyanate-based polyisocyanates containing uretdione and/or isocyanurate groups, as are formed by the catalytic oligomerization of hexamethylene diisocyanate using trialkylphosphines. Among these latter mixtures, particular preference is given to those having a viscosity at 23°C of from 50 to 500 mPa·s and a mean NCO functionality of between 2.2 and 5.0.

The aromatic polyisocyanates, which are likewise suitable in accordance with the invention as isocyanate component (a), but are usually less preferred, are in particular paint polyisocyanates based on 2,4-diisocyanatotoluene or its technical-grade mixtures with 2,6-diisocyanatotoluene or based on 4,4-diisocyanatodiphenylmethane or its mixtures with its isomers and/or higher homologs. Examples of aromatic paint polyisocyanates of this type are the isocyanates containing urethane groups, as are obtained by reaction of excess quantities of 2,4-diisocyanatotoluene with polyhydric alcohols such as trimethylolpropane and subsequent distillative removal of the unreacted diisocyanate excess. Examples of further

aromatic paint polyisocyanates are the trimers of the monomeric diisocyanates mentioned by way of example, i.e., the corresponding isocyanatoisocyanurates, which, following their preparation, are likewise freed from excess monomeric diisocyanates, preferably by distillation.

Also preferred are those polyfunctional isocyanates which, in order to facilitate dispersion in the aqueous phase, are modified at least in part with polyoxyalkylene glycols, such as polyoxyethylene glycol and polyoxypropylene glycol, or with ionic groups. With particular preference, the mass fraction of polyfunctional isocyanates which have been hydrophilically modified in this way is at least 5% of the overall mass of the isocyanate component. Such isocyanates are obtainable by reacting diisocyanates with hydrophilic compounds containing at least two isocyanate-reactive groups and at least one group selected from polyoxyethylene and polyoxypropylene groups and also ionic or ionogenic groups.

For use according to the invention as component (a), particular preference is given to sterically hindered polyisocyanates having 4 to 25, preferably 4 to 16, carbon atoms, which contain in position 2 relative to the NCO group one or two linear, branched or cyclic alkyl groups having 1 to 12, preferably 1 to 4, carbon atoms. Examples thereof are 1,1,6,6-tetramethylhexamethylene diisocyanate, 1,5-dibutylpentamethylene diisocyanate, and p- or m-tetramethylxylylene diisocyanate (TMXDI).

It is of course also possible in principle to use unmodified polyisocyanates of the type mentioned by way of example, provided they conform to the statements made regarding viscosity.

The polyisocyanate component (a) may in addition comprise any desired mixture of the polyisocyanates mentioned.

Any desired resin can be used as alkyd resin (b1). Suitable alkyd resins generally have hydroxyl numbers (OHN, mass of KOH with the same number of OH groups as a unit mass of resin) in the range of 30 to 200 mg/g, pre-

ferably of 50 to 150 mg/g. Especially suitable in accordance with the invention are polyesters modified with any desired fatty acids. They are prepared from saturated and/or unsaturated fatty acids or oils, polyalcohols and polycarboxylic acids. The fatty acids can be replaced at least in part by other monocarboxylic acids. Any desired fatty acids, polyalcohols, and polycarboxylic acids can be used to make the alkyd resins.

10 The term fatty acids includes in general linear or branched monocarboxylic acids having 6 to 35 carbon atoms. The fatty acids may be non-drying or drying. Examples of suitable non-drying fatty acids are, preferably, saturated and monounsaturated, linear or branched aliphatic monocarboxylic acids, with a number of carbon atoms which is preferably from 6 to 18.

Examples of suitable drying fatty acids are unsaturated fatty acids or fatty acid mixtures which comprise at least one monocarboxylic acid having at least two isolated or conjugated double bonds and an iodine number of more than 125 g/(100 g). Preference is given to unsaturated fatty acids having a linear carbon chain of from 16 to 18 carbon atoms.

Specific examples of suitable nondrying fatty acids are 2-ethylhexanoic acid, isononanoic acid, Versatic acid or coconut fatty acid and also oleic acid. Preferred examples of what are understood to be drying fatty acids are unsaturated monocarboxylic acids having an iodine number of more than 125 g (100 g) and 18 carbon atoms. These include, in particular, unsaturated fatty acids having two or three isolated double bonds and various steric configurations, or corresponding polyunsaturated fatty acids with conjugated double bonds. Such fatty acids are present, for example, in natural oils, such as linseed oil, soya oil, safflower oil, cottonseed oil or castor oil, sunflower oil, groundnut oil, wood oil and dehydrated castor oil. The unsaturated fatty acids obtained therefrom are linseed oil fatty acid, safflower oil fatty acid, tall oil fatty acid, cottonseed fatty

acid, groundnut oil fatty acid, wood oil fatty acid, ricinenic fatty acid or sunflower oil fatty acid.

In order to incorporate the fatty acids into the alkyd resins, it is possible on the one hand to esterify
5 the fatty acids with the alcohol components or, on the other hand, to introduce them into the alkyd resin by transesterification reactions of the oils.

It also is possible to employ so-called technical-grade oils as fatty acids, these oils generally being
10 mixtures of cis-linolenic acid, linoleic acid, oleic acid and stearic acid. The technical-grade oils or fatty acids can be employed as such or can be incorporated into the alkyd resin through transesterification reactions or after dehydration reactions (ricinenic fatty acid).

15 Where polyunsaturated fatty acids are used, particular preference is given to employing mixtures of fatty acids containing isolated and conjugated unsaturation, for example having a mass fraction of from 10 to 80% of fatty acids containing conjugated unsaturation.

20 The mass fraction of saturated and unsaturated fatty acids incorporated, based on the mass of the solid resin, is generally from 10 to 80%, preferably from 20 to 70%. Of the mass of saturated and unsaturated fatty acids, with particular preference, from 10 to 60% is accounted
25 for by unsaturated fatty acids containing conjugated double bonds. For nonyellowing resins, saturated monocarboxylic acids or fatty acids containing one or two isolated double bonds are preferred. The fatty acids obtained can be chemically optimized by means of
30 fractional distillation, isomerization or conjugation. In order to modify the properties of the alkyd resin, up to 15% by mass of the unsaturated fatty acids may be replaced by other monocarboxylic acids, such as benzoic acid, tert-butylbenzoic acid, hexahydrobenzoic acid,
35 ethylhexanoic acid or abietic acid.

The monocarboxylic acids which can be used together, at least in part, with the fatty acids are understood as being, for example, alicyclic or aromatic monocarboxylic

acids having 6 to 35 carbon atoms. They may, if desired, be substituted.

Suitable polycarboxylic acids used to make the alkyd resins contain, for example, two or more carboxyl groups on a hydrocarbon structure having, for example, from 4 to 36 carbon atoms. It is also possible to employ the esterifiable derivatives of the polycarboxylic acids, such as anhydrides or methyl esters. The dicarboxylic acids which are preferably employed include linear or branched aliphatic, alicyclic or aromatic in structure.

Suitable examples of dicarboxylic acids and derivatives thereof are phthalic anhydride, isophthalic acid, lower alkyl(C_1 - C_6 -alkyl)-substituted isophthalic acid, dimethyl terephthalate, tetrahydro- and hexahydro-phthalic anhydride, succinic anhydride, methyltetrahydro-phthalic anhydride, fumaric acid, maleic anhydride, adipic acid, 2,2,4-trimethyladipic acid, azelaic acid, sebacic acid, dimerized fatty acids, cyclopentanedicarboxylic acid, 1,3- and 1,4-cyclohexanedicarboxylic acids, norbornenedicarboxylic acid, endoethylenecyclohexanedicarboxylic acid or halogenated dicarboxylic acids, such as chlorophthalic anhydride and hexachloro-endomethylenetetrahydrophthalic anhydride, or mixtures thereof.

Polycarboxylic acids of higher functionality, and their derivatives, such as trimellitic anhydride, pyromellitic anhydride or bisanhydrides, can be incorporated proportionately; preferably, up to 10% of the dicarboxylic acids can be replaced by polycarboxylic acids or derivatives thereof. An appropriate tricarboxylic acid can also be obtained by substituted addition or Diels-Alder reaction of maleic anhydride or (meth)acrylic acid with an unsaturated fatty acid.

Alcohols preferred for the synthesis of the alkyd resins are aliphatic, cycloaliphatic and araliphatic alcohols having 2 to 6 hydroxyl groups and 2 to 24 carbon atoms per molecule and a molar mass of from 62 to 434 g/mol. The alcohols may have primary, secondary and tertiary hydroxyl groups. The linear or branched, substituted

or unsubstituted carbon chain can be interrupted if desired by ether or ester groups.

Examples of the compounds employed as diols are glycols, such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-pentanediol, 1,6-hexanediol, 1,2-decanediol, 2,2-ethylbutyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, cyclohexanedimethanol, 1,1-isopropylidenebis(p-phenoxy)di-1-ethanol, 1,1-isopropylidenebis(p-phenoxy)di-2-propanol, di(hydroxyethyl)-5,5-dimethylhydantoin, and the hydrogenated bisphenols A and F. As ether alcohols use is made, for example, of diethylene glycol, triethylene glycol, dipropylene glycol or tripropylene glycol, and ethoxylated or propoxylated bisphenol A or F products.

Examples of higher-functional polyols are glycerol, trimethylolethane, trimethylolpropane, trimethylolhexane, ditrimethylolpropane, 2,2-dimethylolbutan-3-ol, 2,2-bis(hydroxymethyl)butan-1-ol, pentaerythritol, dipentaerythritol, tripentaerythritol, tris(2-hydroxyethyl)isocyanurate, and also ethoxylated or propoxylated polyhydric alcohols such as trimethylolpropane, pentaerythritol, and sugar alcohols, such as mannitol or sorbitol, and mixtures thereof.

Primary monoalcohols having a chain-terminating action, such as isodecanol, cyclohexanol, benzyl alcohol or fatty alcohols, can be incorporated by condensation in certain fractions, preferably when carboxylic acids having a basicity of more than two are used.

The alkyd resins can be prepared by polycondensation in accordance with known methods, as are described, for example, in S. Paul, *Surface Coatings*, pp. 70 to 139, John Wiley & Sons, New York, 1985, hereby incorporated by reference.

For example, the polycondensation can be carried out by heating in the melt or by an azeotropic method, with elimination of water. The desired number of hydroxyl and acid groups can be introduced by an appropriate choice of the ratios of equivalents, a suitable reaction regime and, if desired, by working in steps. The appropriate

process conditions and solution criteria are familiar to the person skilled in the art.

Any desired hydroxy-functional emulsifiers (b2) can be used in the composition of the invention. Suitable hydroxy-functional emulsifiers include alkylphenols and alkylphenol ethoxylates, alkyl ethoxylates, alkyl glycosides, as described for example in DE 34 04 558, alkyl polysaccharides, sorbitol mono- and diesters, ethoxylated sorbitol esters, sorbitol hexaesters, propylene oxide-ethylene oxide copolymers, polyvinyl alcohols or partially hydrolyzed polyvinyl acetates, and water-soluble hydroxy-functional polymers formed by addition polymerization, condensation polymerization or polyaddition.

Suitable hydroxy-functional polyesters include water-soluble polyesters whose solubility in water derives from the fact that polyethylene glycol has been used as hydrophilic component and/or from the high acid number.

Particular preference is given to hydroxyl-containing polyurethanes or polyurethane-polyureas which can be prepared by reacting polyfunctional isocyanates with, *inter alia*, hydroxy-functional polyesters or polyethers as hydrophobic component, the polyesters being obtained by condensation from the polycarboxylic acids and polyols already described above, and polyethylene glycol and/or dihydroxy acids, for example dimethylolpropionic acid, as hydrophilic components, with or without chain extension using polyamines. These polyurethanes or polyurethane-ureas can be prepared, for example, in bulk or in inert solvents by adding diisocyanates to the hydroxy components or by chain extension of isocyanate-functional prepolymers in the aqueous phase, using polyamines. Attention is directed to copending application Attorney Docket No. 016878/0686, filed on the same date as this application, hereby incorporated by reference, for examples of useful emulsifiers.

In order to prepare the alkyd resin emulsions, these alkyd resins are first of all mixed with the above-described emulsifiers or emulsifier dispersions, in the

presence or absence of the inert solvents described above.

5 Generally, the mixtures comprise from 40 to 97, preferably from 50 to 95, parts by weight of the hydrophobic alkyd resins mentioned in a blend with from 3 to 60, preferably from 5 to 50, parts by weight of the specified emulsifiers or emulsifier dispersions. However, it is often important to select the nature and proportions of the individual components, within the
10 scope of the comments made, such that the mass fraction of ethylene oxide originating from component (b2) in the water-dispersible mixtures is not more than 20%, preferably not more than 15%, of the mass of the solid (b1 + b2).

15 The mixtures can be prepared simply by blending the synthetic resins with the emulsifiers or aqueous emulsifier dispersions, with or without the presence of further solvents, for example hydrocarbons, alcohols, ketones, glycol ethers or N-methylpyrrolidone.

20 The aqueous synthetic-resin dispersions according to the invention are prepared by dispersing the novel mixtures in water, which can be done either simply by stirring water into the initially introduced mixture of the synthetic resins with the emulsifier, using customary
25 dissolvers or stirrers, or else by pouring the mixture into water, with vigorous stirring. If desired, it is possible first to add part of the water to the above-described mixture and then to pour this mixture, with stirring, into the remaining quantity of water. In this
30 way, stable oil-in-water emulsions can be obtained.

To prepare the alkyd resin emulsion, it is also possible first to prepare an aqueous solution of the emulsifier, into which the alkyd resin is then stirred under heavy shearing.

35 The ready-to-use coating compositions can be obtained by emulsifying the polyisocyanate component (a) in the aqueous emulsion of the alkyd resin (b), the alkyd resin emulsion taking over the function of an emulsifier for the added polyisocyanate (a). As polyisocyanate

component (a) it is possible, but generally not preferable, to use hydrophilically modified polyisocyanates which, because of the incorporated ionic or nonionic hydrophilic centers, are autodispersible.

5 Thorough mixing can be achieved simply by stirring, generally, at room temperature. In this context, the quantity of polyisocyanate component is calculated such that the resulting ratio of the number of isocyanate groups of component (a) to the number of alcoholic
10 hydroxyl groups of component (b) is generally from 0.3:1 to 5:1, preferably from 0.5:1 to 4:1 and, with particular preference, from 0.8:1 to 3:1.

 Prior to the addition of the polyisocyanate component (a), it is possible to incorporate into the externally
15 emulsified alkyd resin emulsion (b), the auxiliaries and additives which are customary in coating technology. These auxiliaries and additives may also be present in the polyisocyanate component (a).

 If desired, the dispersions according to the invention can be modified, prior to, during or after their
20 preparation, by the addition of other polymers, for example polyacrylates, polyurethanes, hard resins or polyesters in solution or dispersion form. If the additional binders carry reactive groups, for example
25 hydroxyl groups, then these groups should be taken into account in connection with the mixing ratio of components (a) and (b).

 The coating compositions according to the invention include the above-described usually hydroxyl-containing,
30 water-dispersible binders and the isocyanates. As auxiliaries and additives they can also comprise, for example, pigments, fillers, coatings additives, emulsifiers which are preferably incorporated into the network via reactive double bonds or hydroxyl groups
35 during film formation, especially nonionic emulsifiers, leveling agents, antifoams, rheological auxiliaries, catalysts, siccatives and further binders. The purpose of the additives is to influence coatings properties such as, for example, curing times and surface quality, or to

influence applications-related properties, for example the viscosity.

In order to achieve ready dispersibility of the polyisocyanates it is possible to establish a suitable, low viscosity. This goal is also served by dissolving highly viscous or solid polyisocyanates in water-miscible organic solvents which react slowly or not at all with isocyanates. Examples of useful unreactive solvents are glycol dialkyl ethers, such as glycol dimethyl ether, esters, such as ethylglycol acetate, ketones, such as acetone, cyclic ethers, such as dioxane, or lactams, such as N-methylpyrrolidone. Preference is given to alcohols containing sterically hindered alcohol groups, ketone alcohols or alkoxy alcohols, such as butoxyethanol, butyldiglycol, methoxyisopropanol or diacetone alcohol. They are used, shortly before processing and without heating, to prepare a polyisocyanate solution which has a solids content of more than 40% by mass, preferably from 50 to 95% by mass, with a viscosity of from 0.5 to 2000 mPa·s, preferably from 1 to 20 mPa·s.

Suitable pigments are the customary pigments, for example those described in DIN 55 944: preferably carbon black, titanium dioxide, finely disperse silica, aluminum silicate, metal powders or flakes, organic and inorganic color pigments, anticorrosion pigments, such as lead compounds and chromate compounds, and metal-effect pigments. In addition to the pigments and fillers it is possible if desired to employ customary organic dyes. It is likewise possible to add proportions of crosslinked organic microparticles.

The methods for preparing the coating compositions from the individual components are known. For example, it is possible to disperse the pigments in a particularly appropriate grinding resin and, if desired, to mill them to the required particle size. Another procedure envisages milling the pigments in the aqueous dispersion of the binder component (b).

In this context care should be taken to ensure that the stability of the aqueous dispersion remains

unaffected during the milling process. Following the dispersion of the pigments it is possible to add further binder components. These may comprise the externally emulsified alkyd resins of the invention and, if desired, other binders of those described above. If desired, further coatings auxiliaries can be added in order to influence properties such as, for example, dispersibility.

In accordance with another preferred procedure, the externally emulsified alkyd resins or, if desired, other customary paint resins are first of all mixed with a little water, with or without the addition of fillers, pigments, colorants and the like, and this mixture is dispersed on a roller bed or in a ball mill, to form pastes. These pastes can then be diluted with water and, if desired, admixed with further resin emulsion and additives to prepare the ready-to-use coating formulations.

If desired, pigments or coatings auxiliaries may also be present in component (a). This coatings component is generally nonaqueous. However, it is dispersible in the aqueous alkyd resin emulsion. It may if desired contain small fractions of organic solvents in order to establish an appropriate viscosity for dispersion. Care should be taken to ensure that the additives are unable to react with the isocyanate component. The brief mixing of isocyanates with alcohols, such as butoxyethanol or diacetone alcohol, is possible.

The coating compositions according to the invention can be applied to the materials to be coated in any desired manner, such as using customary techniques, for example dipping, spraying or rolling. The applied film subsequently crosslinks.

Crosslinking of the coating can be effected at temperatures of, for example, from 0°C to 150°C. The coating compositions according to the invention can advantageously be cured at relatively low temperatures, for example at temperatures between 10°C and 80°C,

especially below 60°C. If appropriate, a flash-off time can be allowed to elapse before crosslinking.

The thicknesses of the coats applied depend on the intended use of the coating composition. For example, clearcoats generally have a thickness of up to 60 μm , pigmented basecoats or topcoats generally have a thickness of from 10 to 50 μm , coatings as fillers or stone-chip resistance coats a thickness generally from 30 to 100 μm , and anticorrosion primer coatings generally a thickness of from 20 to 70 μm .

The coating composition according to the invention is suitable for single-coat finishes, topcoats and primers.

Any desired substrates can be suitably coated in accordance with the invention, examples being metal substrates such as iron, aluminum or zinc, nonmetallic substrates, such as mineral substrates (e.g., concrete, glass), wood, plastics substrates, such as polyolefins, polycarbonates and polyurethanes, and, if desired, substrates provided with a preliminary coating. Application can be made to a dried or crosslinked coated substrate. It also is possible to operate by the "wet-on-wet" method. For this purpose the coating composition of the invention can be applied, if desired after a short flash-off phase, to a substrate provided with a noncrosslinked coating composition. It is also possible to apply a further coating composition to the novel coating composition, without drying or crosslinking beforehand and, if desired, after a short flash-off phase. The further coating composition may comprise a coating composition on the basis of the present invention or another coating composition. Subsequently, the coating films are crosslinked together.

The coating composition according to the invention is particularly suitable for use in multi-coat finishing, with at least one coat being prepared using the coating composition of the invention. In this context it is possible, depending on the pigmentation, to produce, for example, clearcoat compositions, basecoat or topcoat

compositions and also stone-chip resistance compositions, fillers or primers. A preferred use is that as clearcoat compositions applied to a basecoat which is based on an aqueous solvent-containing coating composition. The coatings thus obtained are distinguished by high mar resistance, a high gloss retention capacity and enhanced resistance properties.

The examples which follow illustrate the invention, but do not limit it. All contents, parts and numerical percentages below are fractions by mass unless otherwise specified.

EXAMPLES

Hydroxy-functional emulsifier E1

26.8 g of dimethylolpropionic acid are suspended at about 80°C in 100 g of polyethylene glycol 1000 (mean molar mass M_n about 1000 g/mol). Then, after heating to 70°C, 51 g of tetramethylxylene diisocyanate (TMXDI) and 36.6 g of tolylene diisocyanate (TDI) are added dropwise at a rate such that the temperature does not exceed 70°C (about 30 min). Once all of the isocyanate has been added, the admixture is stirred at the temperature for one hour and the reaction temperature is then raised to 90°C. The temperature is maintained until the isocyanate content has fallen to 3.8%. Then 30 g of Genapol® O-100 (ethoxylated fatty alcohol) and 60 g of a polyester made from isophthalic acid, adipic acid, neopentylglycol and trimethylolpropane (OH number 107 mg/g, acid number 3 mg/g) are added and the mixture is stirred at 90°C until the NCO content has fallen to 1.4%. Then, with vigorous stirring, 400 g of heated deionized water are added over the course of 10 minutes. This is followed directly by the rapid (about 5 min) dropwise addition of 3.75 g of triethylenetetramine dissolved in 37.5 g of deionized water. Following the addition of 4.5 g of triethylamine and a reaction time of 3 hours at 80°C, a further 4.4 g of triethylamine and

1000 g of deionized water are added and the mixture is then cooled. A pastelike dispersion is obtained.

Alkyd resin emulsion A1

220 g of the above-described emulsifier emulsion E1
5 are added to 200 g of a commercial alkyd resin having an oil content of 34% (e.g., Alftalat® AF 342 100%) and the mixture is stirred at 70°C for about 60 min until it is homogeneous.

After adding 1 ml of ammonia water (25%), 70 g of
10 deionized water heated at 70°C are added dropwise very slowly with vigorous stirring (about 2 hours). A milky, pseudoplastic dispersion is obtained.

Alkyd resin emulsion A2

40 g of Genapol® O-100 (ethoxylated fatty alcohol)
15 and 10 g of butylglycol are added to 200 g of a commercial alkyd resin having an oil content of 42% (e.g., Alftalat® AM 424 100%) and the mixture is stirred at 70°C for about 60 min until it is homogeneous.

After adding 2 ml of ammonia water (25%), 230 g of
20 deionized water heated at 70°C are added dropwise very slowly with vigorous stirring (about 4 hours). A milky dispersion is obtained.

Coating composition

19.5 g of the externally emulsified alkyd resin
25 emulsion A1 are diluted with 2 g of methoxypropyl acetate and mixed with 6 g of a polyisocyanate (Bayhydur® LS 2980). The pot life of this mixture is more than 4 hours. The films, cured at room temperature, were free from tack, clear and crosslinked and exhibited good
30 evenness. After drying at 80°C for 30 minutes and at 60°C for 16 hours, pendulum hardnesses of more than 100 s were measured, which rose to more than 150 s after a further week at room temperature. The solvent resistance (xylene, 5 minutes) of the films cured in this way was
35 excellent.

Similar results are obtained with the alkyd resin emulsion A2.

Although only a few exemplary embodiments of this invention have been described in detail above, those
5 skilled in the art will readily appreciate that many modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of this invention. Accordingly, all such
10 modifications are intended to be included within the scope of this invention.

